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PVA-CONTAINING COMPOSITIONS

The present invention relates to PVA-containing compositions, particularly filled compositions.  
5 Methods of making such compositions and methods of extruding PVA-containing compositions  
are also disclosed.

There is currently a significant and increasing demand for bio-degradable polymers, to replace  
non bio-degradable polymers which take up an ever greater amount of disposal space, such as  
10 land-fill, or need to be incinerated.

Polyvinylalcohol (PVA) is one bio-degradable polymer which is in widespread use. As a film,  
PVA shows a high degree of impermeability to a number of gases. Incorporated into adhesive,  
PVA shows high adhesive strength. PVA has significant potential in a wide range of products.  
15 However, the applications of PVA have been limited because there is currently no formulation of  
PVA or PVA-containing composition which can readily be extruded.

While attempts have been made to extrude articles from PVA, it has been found that melt  
extruded PVA becomes very unstable and significant residues become adhered to the surfaces of  
20 the extrusion apparatus, requiring very careful control of process conditions, specialised extrusion  
apparatus and frequent shut down of the extrusion process and purging of the apparatus.

It is known to polymerize ethylene with vinylalcohol to provide a copolymer of ethylene-  
vinylalcohol, in an attempt to retain the desirable properties of PVA whilst simultaneously  
25 obtaining an extrudable polymer. One such copolymer is marketed under the trade mark  
SOARNOL (registered trade mark of the Nippon Synthetic Chemical Industry Co, Limited).  
However, it is found that this copolymer has effectively lost all of the advantageous properties of  
PVA and is not an effective alternative to an extrudable PVA.

30 A chemically modified PVA is also known and sold as VINEX (registered trade mark of Air  
Products). This suffers, however, from the fact that some of the advantageous PVA

properties are adversely affected by the chemical modification.

The search for bio-degradable polymers is acute in relation to certain sanitary products such as  
diapers and sanitary towels. However, these products typically comprise superabsorbent materials  
5 and at present such materials are only available in combination with conventional non bio-  
degradable polymers.

There are disclosed herein PVA-containing compositions, methods of manufacturing the same  
and methods of extruding PVA-containing compositions which overcome or at least ameliorate  
10 some of the disadvantages identified in the art.

Aspects of the invention are set out in the independent claims.

There is disclosed herein a PVA-containing composition comprising a blend of PVA and an  
15 amount of lubricant effective to render the blend extrudable.

The lubricant preferably comprises a fatty acid amide and the composition further comprises a  
plasticiser, the resultant blend being suitable for extrusion in conventional melt-extrusion  
apparatus. In embodiments disclosed herein, a PVA-containing composition comprises 8 to 15%,  
20 plasticizer and 0.5 to 1.5% internal lubricant, by weight.

The above composition is thus an extrudable PVA-containing polymer, typically with a flexural  
modulus similar to other extrudable polymers. Known advantageous properties of PVA, such as  
its high tensile strength, good puncture resistance, and good barrier characteristics are retained in  
25 an extrudable composition which can be processed on current extrusion lines, blow-moulders and  
injection moulders without modification, and without the processing problems such as thermal  
degradation and high temperature cross linking, observed in attempts to extrude articles using  
hitherto known PVA-containing compositions.

30 In embodiments disclosed herein, extrudable PVA-containing compositions have been

obtained comprising fully hydrolysed PVA as well as partially hydrolysed PVA, and including PVA that is 70% or more hydrolysed.

5 Further embodiments disclosed herein provide PVA-containing compositions in which the molecular weight of the PVA varies from around 20,000, in some cases from around 10,000, to greater than 150,000. Generally, the application of the disclosed technique is not limited to PVA of any particular percent hydrolysis nor of any particular molecular weight.

10 The filled PVA-containing composition disclosed herein comprises a blend of PVA plus filler. In this composition, the filler is effectively a bulking agent and is relatively inexpensive compared to the PVA, thus a composition is obtained retaining advantageous properties of PVA whilst being cheaper per unit weight to produce.

15 Preferably the PVA-containing compositions are provided in the form of pellets or tablets. These preferably have a size of between about 1mm and 5mm in diameter and are suitably obtained by a method in which PVA, preferably substantially uncompounded and in powder or granular form, is mixed with lubricant and filler and other compounding ingredients, and cold pressed to form a tablet or pellet. This cold-pressing method is substantially as described in WO-A-98 /26911 in relation to different polymers.

20 With this method, the ingredients can be uniformly mixed and compounded in the correct proportions for the final product, and made into a form that is easier to handle than powder. In addition, since the mixture is cold pressed rather than melted, problems of thermal degradation or variation in properties are reduced.

25 References to "cold pressing" are intended to imply applying pressure to the powder to cause agglomeration without substantial melting of the polymer. The temperature is preferably less than about 100 degrees Celsius, more preferably less than about 70-80 degrees Celsius. Preferably heat is not applied directly to the mixture. However, heat may be generated by mixing and/or  
30 pressing, and this may be allowed to warm the mixture, or cooling may be provided. It is permissible for some heat to be applied directly if necessary to facilitate

binding. Some melting of the polymer or other ingredients may occur, particularly on a microscopic scale as a result of pressure at the interface between adjacent particles, but it is important that the bulk of the polymer granules do not liquefy.

- 5 Preferably, the mixture is compressed in discrete quantities into tablets or pellets, for example in a tablet press; this may provide more reliable agglomeration.

However, it is possible for the mixture to be extruded under pressure through an orifice, the pellets forming following exit of the mixture from the orifice. In such a case, binder or moisture  
10 may be added to the mixture, preferably as the mixture is extruded, or after preliminary mixing of the constituents.

Preferably, the mixture is substantially dry, but includes sufficient residual moisture to bind the tablets or pellets on pressing. This avoids the need to add a separate binder, and allows the tablets  
15 or pellets to be broken more easily as they enter the extruder simply by drying them further. When water is relied upon for binding, it is desirable to ensure that the tablets or pellets are dried prior to extruding, for example at between 40 and 80 degrees Celsius for 4-8 hours; this alleviates problems of vapour formation during extrusion. The moisture content is desirable to form the tablets, but after forming, the tablets should in most cases retain their shape even when dried.

20 Preferably, the moisture content is less than about 10% by weight, and preferably greater than 0.01 % by weight, more preferably less than about 5%. If the pellets or tablets are extruded or otherwise formed at relatively low pressures, however, the moisture content may be about 20% or even higher to ensure binding. If the pellets are too moist, they may tend to stick together,  
25 inhibiting flow, and drying after forming may be desirable.

The moisture may comprise residual moisture in the polymer or in one or more of the compounding ingredients. In this way, moisture can be provided automatically simply by not drying the ingredients fully prior to mixing.

30 It is preferred that the filled PVA-containing composition is extrudable, and hence

the filled PVA-containing composition further comprises an effective amount of a lubricant to render the composition extrudable. The lubricant suitably comprises a fatty acid amide or a plasticiser or a mixture of both a fatty acid amide and a plasticiser.

5

The lubricant in compositions disclosed herein is provided so as to improve the thermal stability of the composition under extrusion. The lubricant may be referred to as an internal lubricant, in that its function is to improve lubrication between the polymer chains. Compositions disclosed herein may be intended for use in or in connection with food stuffs, and hence it is preferred that  
10 the lubricant is approved for food use. It is further preferred that the lubricant is a fatty acid amide, and particularly a straight or branched C<sub>12</sub>-C<sub>24</sub> fatty acid amide, more particularly C<sub>16</sub>—C<sub>20</sub>. Particularly and surprisingly good results are obtained if the lubricant comprises stearamide, a straight chain C<sub>18</sub> fatty acid amide.

15 The compositions disclosed herein further include a plasticiser, to lower the melt temperature of the polymer under extrusion. The plasticiser may suitably be selected from glycerine, ethylene glycol, triethylene glycol, low molecular weight polyethylene glycols and low molecular weight amides. A particularly preferred plasticiser comprises or consists of glycerol.

20 While the proportion of components present may vary in compositions disclosed herein, embodiments disclosed herein generally comprise, by weight, 20 to 50% filler and 0.5 to 1.5% internal lubricant. More particular embodiments disclosed herein comprise, by weight, 20–50% filler, 40-70% PVA, 0.5 to 1.5% internal lubricant and 8-15% plasticizer.

25 Compositions disclosed herein are thus extrudable, but it may be that ease of extrusion depends partly upon the state of the extrusion apparatus, in particular the roughness of surfaces in the apparatus. The composition further comprises an additional lubricant, which may be referred to as an external lubricant, to prevent or reduce adhesion of the composition to such surfaces. This external lubricant is present at 0.001 to 0.1 % by weight of the composition and preferably  
30 approved for food use, in the same way as the internal lubricant. Stearate salts are suitable external lubricants, in particular magnesium, lead or zinc stearates.

Fillers for incorporation into compositions disclosed herein may suitably be selected from conventional polymer fillers. Typically the filler is an inert, inorganic material and a particularly preferred filler is or comprises talc, calcium carbonate. In a specific embodiment disclosed herein, this talc may be micronised, such as in particles with a mean size of about 20 microns and may further be coated, such as with a stearate. One such coated, micronised talc is available from Croxton and Gary as 90T (trade mark of Croxton and Gary).

It is further an option for the filler to comprise or consist of a superabsorbent material. In a specific example described below, a filled PVA-containing composition comprises a superabsorbent which contains cross-linked sodium polyacrylate (available from Alloid Colloids as SALISORB CL31 (registered trade mark)). Filled compositions disclosed herein may nevertheless contain superabsorbent material of substantially any type. Incorporation of such superabsorbent material confers the particular advantage that sanitary products such as diapers and sanitary towels, hitherto major components of waste storage sites such as land-fill sites, may now be made of or comprise a significant proportion of bio-degradable material.

A number of water-absorbent compositions are known and suitable for use as the filler. For example, US Patent numbers 3,954,721 and 3,983,095 disclose preparations for derivatives of copolymers of maleic anhydride with at least one vinyl monomer in fibrous form. The fibrous copolymers are rendered hydrophilic and water-swellaable by reaction with ammonia or an alkali metal hydroxide. US Patent No. 3,810,468 discloses lightly cross-linked olefin-maleic anhydride copolymers prepared as substantially linear copolymers and then reacted with a diol or a diamine to introduce cross-linking. The resultant lightly cross-linked copolymers are treated with ammonia or an aqueous or alcohol solution of an alkali metal hydroxide. US Patent No. 3,980,663 describes water-swellaable absorbent articles made from carboxylic polyelectrolytes via cross-linking with glycerine diglycidyl ether. These patents are incorporated herein by reference.

European Published Application No. 0 268 498 (incorporated herein by reference) describes a water-absorbent composition formed by causing a substantially linear polymer of water-

soluble ethylenically unsaturated monomer blends comprising carboxylic and hydroxylic monomers to cross-link internally.

Further examples of water-absorbent compositions are those produced from a copolymer  
5 of an  $\alpha,\beta$  unsaturated monomer having at least one pendant unit selected from a  
carboxylic acid group and derivatives thereof and a copolymerisable monomer. A  
proportion of the pendant units are present in the final copolymer as the free acid and  
a proportion as the salt of the acid. These copolymers are capable of being cross-linked,  
either internally or with a variety of cross-linking agents, to form the water-swellable  
10 composition. Examples of water-swellable compositions of this type can be found in US  
Patent Nos 4,616,063, 4,705,773, 4,731,067, 4,743,244, 4,788,237, 4,813,945,  
4,880,868 and 4,892,533 and European Patent Nos 0 272 074 and 0 264 208 and  
European Published Application No. 0 436 514 which are incorporated herein by  
reference.

15

Derivatives of carboxylic acid groups include carboxylic acid salt groups, carboxylic acid  
amide groups, carboxylic acid imide groups, carboxylic acid anhydride groups and  
carboxylic acid ester groups.

20 Other examples of water-absorbent compositions can be found in US 4798861,  
WO93/17066, WO93/255735, WO 93/24684, WO93/12275, European Published  
Application Nos 0 401 044, 0 269 393, 0 326 382, 0 227 305, 0 101 253, 0 213 799,  
0 232 121, 0 342 919, 0 233 014, 0 268 498 and 0 397 410, British Patent Application  
Nos 2 082 614, 2 022 505, 2 270 030, 2 269 602 and 2 126 591, US Patent Nos  
25 4,418,163, 4,418,163, 3,989,586, 4,332,917, 4,338,417, 4,420,588 and 4,155,957 and  
French Patent Application No. 2 525 121 which are all incorporated herein by reference.

The extrudable compositions disclosed herein are suitable for manufacture of  
substantially any article made using currently extrudable polymers, including films and  
30 bottles and any other articles. The compositions are suited to manufacture of filaments  
and fibre, for use in spunbond, non-woven and melt-blown applications. The  
composition is suitable also for manufacture of such articles as agri-chem sachets, mulch  
films, plant pots, domestic bags, diapers, drinking straws, fem care products, hangers,  
incontinence pads, sachets, six pack



rings, disposable clothing, expanded foams, gloves, film canisters, golf tees, shot gun cartridges, bed pans, bottles, bowls, cotton buds, hospital curtains, 'one-use" sterile products and packaging materials.

- 5 Particularly good results have been obtained with PVA-containing compositions having the following make-up, by weight:

- (a) 40 to 70% PVA;
- (b) 20 to 50% filler, preferably a micronised inorganic material such as talc, preferably  
10 coated with stearate;
- (c) 8 to 15 % plasticizer, preferably glycerol;
- (d) 0.5 to 1.5 % internal lubricant, preferably a fatty acid amide, most preferably octadecanamide; and
- (e) 0.0001 to 0.1 % external lubricant, preferably stearate.

15

The composition may contain residual moisture, sufficient to enable the composition to be bound as a cold-pressed tablet.

Further advantageous results have been obtained in compositions of the invention

- 20 comprising, by weight:-
- 50 to 60% PVA;
  - 30 to 40% stearate-coated calcium carbonate;
  - 8 to 15% glycerol;
  - 0.5 to 1.5% octadecanamide; and
  - 0.0001 to 0.1% zinc stearate.

25

There is also disclosed herein a method of making an extrudable PVA-containing composition comprising blending PVA with a lubricant and a filler, said lubricant including a fatty acid amide. The method preferably comprises blending PVA with a fatty acid amide in the presence of an amount of moisture sufficient to bind the composition into tablets or pellets upon cold  
30 pressing.

The amount of lubricant blended with the PVA is typically restricted by the fact that, above a certain percent, excess lubricant separates out from the blend, and lubricant is

blended 0.5 to 1.5% by weight of the PVA present. The method thus conveniently enables tablets or pellets of the composition to be prepared as the feedstock for an extrusion. Blending of the components of the composition is achieved using conventional apparatus, one such example being a high speed blender.

5

The method may optionally comprise adding small amounts of moisture to the components to be blended, such as by dripping water into the blend. Preferably, PVA and lubricant are fed into a high speed mixer gravimetrically.

10 There is also disclosed herein a method of making a PVA-containing composition comprising blending PVA, a lubricant and a filler, wherein the filler comprises a superabsorbent material. It is preferred that blending is carried out in the presence of sufficient moisture to bind the composition into tablets or pellets upon cold pressing, the moisture optionally being present in the starting materials of the blend or being introduced into the blend, such as by drip-feeding.

15

There is also disclosed herein a method of extruding a PVA-containing composition so as to form an extruded product which contains PVA, comprising:

20 blending PVA with a lubricant and a filler;  
and

cold pressing the resultant blend into pellets or tablets;

25 wherein the pellets or tablets comprise the polymer feedstock for extrusion of an  
extruded product containing PVA.

30 The PVA is preferably blended with one or more lubricant and filler components in the presence of sufficient moisture to bind the blend upon cold pressing. An advantage of the method is that the PVA-containing feedstock for the extrusion step is obtainable substantially without melting of the PVA. This improves the stability of the PVA during subsequent extrusion. Hitherto, as has been recognised by the present inventor, attempts to extrude a PVA-containing feedstock largely failed as the PVA already had a heat history, ie had been

wholly or partially melted in processing stages prior to the extrusion stage. The technique disclosed herein avoids the disadvantage of introducing such a heat history into the PVA—containing composition.

5 There is also disclosed herein a method of extruding a PVA-containing composition comprising blending PVA, a lubricant and a filler to form a feedstock for an extrusion process, the feedstock being in the form suitably of powder, pellets or tablets, and extruding the feedstock into a product, wherein the feedstock is prepared substantially without melting of the PVA.

10 There is also disclosed herein a method of extruding a polymer composition containing a heat sensitive polymer, comprising blending the heat sensitive polymer with a filler and a lubricant to form a feedstock for an extrusion process, the feedstock being suitably in the form of powder or pellets or tablets, and extruding the feedstock into an extruded product, wherein the feedstock is prepared substantially without melting of the heat sensitive polymer.

15 Optional and preferred features mentioned above are optional and preferred features of all techniques disclosed herein.

The invention is now described in the following non-limiting examples.

20

Example 1

A blend of, by weight, approximately 60% fully hydrolysed PVA, 30% calcium carbonate, 10% glycerol, 0.01 % zinc stearate and 1 % octadecanamide was prepared in  
25 a high speed blender. It was found to have a white/cream colour with the following properties: -

density	1.65 g/cm <sup>3</sup>
melt density	1.46 g/cm <sup>3</sup> at 200 <sup>0</sup> C (under ISO 1183)
30 MFR	357 (10 mins/200 <sup>0</sup> C/21.6 kilograms, under ISO 1133)
melt temperature	200 <sup>0</sup> C

processing temperature	190 - 200°C
residence time	up to 15 minutes
drying time	4 hours at 80°C

### Example 2

A blend was prepared in a similar way to example 1 of, by weight, approximately 60% partially hydrolysed PVA, 30% calcium carbonate, 10% glycerol, 0.01% zinc stearate and 1% octadecanamide. This was found to have the following properties:-

density	1.65 g/cm <sup>3</sup>
melt density	1.38-1.40 g/cm <sup>3</sup> at 190°C (under ISO 1183)
MFR	22 (10 mins/190°C/5 kilograms, under ISO 1133)
apparent melt viscosity	236/49 (Pa.s 1,000s/10,000s)
melt temperature	200°C
processing temperature	190-200°C
residence time	up to 15 minutes
drying time	4 hours at 80°C

### Example 3

The PVA-containing compositions of examples 1 and 2 were examined for their extrudability in injection-moulding machines made by Brabender, Killion, Windsor, Hesas, Battenfield, Fischer, Demag and Arburg. Extrusion processing was carried out using a single full flight screw with constant pitch. The barrel temperature had a profile of 180-200°C (melt 190-210°C) and the screw speed varied typically between 20 and 120 rpm. Shut down of the apparatus was carried out by maintaining the temperature for up to 15 minutes with screw rotation stopped, over a period of 3 hours reducing the temperature to 100°C with screw rotation stopped and subsequently completing the shut down by turning the machine off.

The compositions of both examples 1 and 2 were satisfactorily extruded into a range of films and tubes blow-moulded containers of various sizes and colours and injected moulded

products.

Examples 4-9

PVA-containing compositions were prepared as blends of the following components in the amounts shown:-

<u>EXAMPLE</u>						
	4	5	6	7	8	9
<u>Components</u>						
PVA - fully hydrolysed	-	-	-	50	60	55
PVA - partially hydrolysed	50	60	55	-	-	-
Calcium carbonate (coated)	40	30	30	40	30	30
Glycerol	9	9	14	9	9	14
Octadecanamide	1	1	1	1	1	1
Zinc Stearate	0.01	0.01	0.01	0.01	0.01	0.01

Example 10

A further filled PVA-containing compositions was prepared as a blend of, by weight, approximately 60% partially hydrolysed PVA, 30% cross-linked sodium polyacrylate (a superabsorbent), 9% glycerol, 1% octadecanamide and 0.01% zinc stearate.

As far as extrusion apparatus is concerned, it is advantageous to use chrome plated screws and for the melt flow path to use chrome plated surfaces and gradual tapers to streamline the melt.

- 5 The invention thus provides PVA-containing compositions for use in the manufacture of bio-degradable articles.

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CLAIMS

1. A PVA-containing composition comprising, by weight:  
40 to 70% PVA;  
20 to 50% filler;  
8 to 15% plasticizer;  
0.5 to 1.5% internal lubricant; and  
0.0001 to 0.1 % external lubricant.
2. A filled PVA-containing composition comprising, by weight:  
40 to 70% PVA;  
8 to 15% plasticizer;  
0.5 to 1.5 % internal lubricant;  
0.0001 to 0.1 % external lubricant; and  
a filler.
3. A composition according to Claim 1 or Claim 2 wherein the internal lubricant comprises a fatty acid amide.
4. A composition according to Claim 3 wherein the fatty acid amide is a straight or branched  $C_{12}$ - $C_{24}$  fatty acid amide.
5. A composition according to any of Claims 1 to 4, wherein the plasticiser is selected from ethylene glycol, glycerine, glycerol, triethylene glycol, low molecular weight polyethylene glycols and  $C_2$ - $C_8$  amides.
6. A composition according to any preceding claim, in the form of a tablet or pellet obtainable by cold-pressing.
7. A composition according to any preceding claim wherein the filler comprises inert, inorganic material.
8. A composition according to any preceding claim wherein the filler comprises a superabsorbent material.

9. A composition according to Claim 7 wherein the inorganic filler comprises calcium carbonate.

5 10. A composition according to any preceding claim wherein the external lubricant comprises a stearate.

11. A composition according to Claim 1 comprising, by weight:-

50 to 60% PVA;  
10 30 to 40% stearate-coated calcium carbonate;  
8 to 15% glycerol;  
0.5 to 1.5% octadecanamide; and  
0.0001 to 0.1% zinc stearate.

15 12. A composition substantially as herein described with reference to the Examples.

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